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13. ABSTRACT (Maximum 200 words) In this final report we summarize our computational efforts addressing the thermal decomposition of 3-nitro-1,2,4-triazol-5-one (NTO) and hexahydro-1,2,3-trinitro-1,3,5 triazine (RDX). These efforts expand our earlier work on the common explosive 2,4,6-trinitrotoluene (TNT), which has been described in Report AL-TR-90-004 (32 pages). We also report on the dimethylnitramide (DMNA) decomposition, bonding properties of bridged hydrogens, and a superacid solvation model. Tautomerism is the common thread in the studies on NTO and RDX, which are summarized in sections 1 and 2, respectively. In section 6 we expand the earlier reported imine - enamine, keto - enol, and nitro - sci-nitro, tautomerisms with the nitroso - oxime tautomerism using GZ theory with specific inclusion of the effects of solvent molecules. Isotope effects are often used as indicator of the decomposition mechanism for the expulsion of nitro groups. Hence, we report the deuterium kinetic isotope effects for decomposition of dimethylnitramine using density functional theory. This is summarized in section 3. Supercid initiated electrophilic nitrostion reactions are intriguing processes, which are, however, not modeled conveniently because of solvation (protonation) effects. Therefore, we developed a computational model that determines			
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Dr Lammertsma/University of Alabama

the superacid solvation effect on bases and electrophiles. This is summarized in section 5. In the course of many studies we became interested in H-interaction energies and bonding features. We decided to revisit the well established 3 center , 2 electron interaction system which underlies many non-classical bonding arrangements. This fundamental work is summarized in section 4. Most of these studies have been completed successfully. All but one have appeared in the literature. These will therefore discussed only in a summary fashion. A more detailed presentation is given in Appendix A for the nitroso - oxime tautomerism.

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RE: Final Report on Grant AFOSR F19620 94-1-0451 (2+9 pages)

Dear Mike:

As discussed recently by telephone, please find attached to this letter and for your approval the final report on the named grant, entitled "*Insensitive High Explosives – A Computational Study*."

The hard copy will contain Appendix A, which is a complete manuscript.

It is not clear to me whether I or you have to complete Standard Form 298 and whether there are other forms relating to the final report to be completed.

I am looking forward to hearing from you by fax or e-mail on the next step to take..

Sincerely yours,

Koop Lammertsma
Professor of Chemistry

Insensitive High Explosives - A Computational Study**AFOSR F49620-94-1-0451**

Program Director: Dr. Michael R. Berman

Final Report

October 1, 1994 - December 31, 1997

prepared
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INTRODUCTION

In this final report we summarize our computational efforts addressing the thermal decomposition of 3-nitro-1,2,4-triazol-5-one (NTO) and hexahydro-1,2,3-trinitro-1,3,5 triazine (RDX). These efforts expand our earlier work on the common explosive 2,4,6-trinitrotoluene (TNT), which has been described in Report AL-TR-90-004 (32 pages). We also report on the dimethylnitramide (DMNA) decomposition, bonding properties of bridged hydrogens, and a superacid solvation model.

Tautomerism is the common thread in the studies on NTO and RDX, which are summarized in sections 1 and 2, respectively. In section 6 we expand the earlier reported imine \leftrightarrow enamine, keto \leftrightarrow enol, and nitro \leftrightarrow aci-nitro, tautomerisms with the nitroso \leftrightarrow oxime tautomerism using G2 theory with specific inclusion of the effects of solvent molecules.

Isotope effects are often used as indicator of the decomposition mechanism for the expulsion of nitro groups. Hence, we report the deuterium kinetic isotope effects for decomposition of dimethyl-nitramine using density functional theory. This is summarized in section 3.

Superacid initiated electrophilic nitration reactions are intriguing processes, which are, however, not modeled conveniently because of solvation (protonation) effects. Therefore, we developed a computational model that determines the superacid solvation effect on bases and electrophiles. This is summarized in section 5.

In the course of many studies we became interested in H-interaction energies and bonding features. We decided to revisit the well established 3 center 2 electron interaction system which underlies many non-classical bonding arrangements. This fundamental work is summarized in section 4.

Most of these studies have been completed successfully. All but one have appeared in the literature. These will therefore discussed only in a summary fashion. A more detailed presentation is given in Appendix A for the nitroso \leftrightarrow oxime tautomerism.

TECHNICAL DISCUSSION

1. NTO

Published in: N.J. Harris and K. Lammersema, *Tautomerism, ionization, and bond dissociations of 5-nitro-2*A*-dihydro-3*H*-1,2,4-triazolone*, *J. Am. Chem. Soc.* 118, 8048 - 8055 (1996).

The more salient points are summarized:

Tautomerization, ionization, and bond dissociations of the insensitive high-energy explosive 5-nitro-2,4-dihydro-3*H*-1,2,4-triazolone (NTO, 1) were studied by molecular orbital SCF and MP2 theories and with the Becke3LYP hybrid density functional using the 6-31+G* and 6-311+G** basis sets. Energies computed with these methods were compared against accurate G2 energies for the tautomerization, ionization, and bond dissociations of nitromethane. An important outcome from the present study is our finding that the B3LYP hybrid density functional is an accurate and computationally efficient method for computing energies and geometries on large molecules. Both MP2/6-311+G** and B3LYP/6-311+G** gave satisfactory energies for tautomerization, ionization and bond dissociations of the small model system, nitromethane. On the other hand, SCF theory is not adequate especially for computing bond dissociation energies.

The B3LYP/6-31+G* and MP2/6-31+G* geometries for the NTO anion **9** compare well with the reported X-ray structure of the NTO diaminoguanidinium salt. The harmonic vibrational frequencies calculated with Becke3LYP compare well with those observed for crystalline NTO.

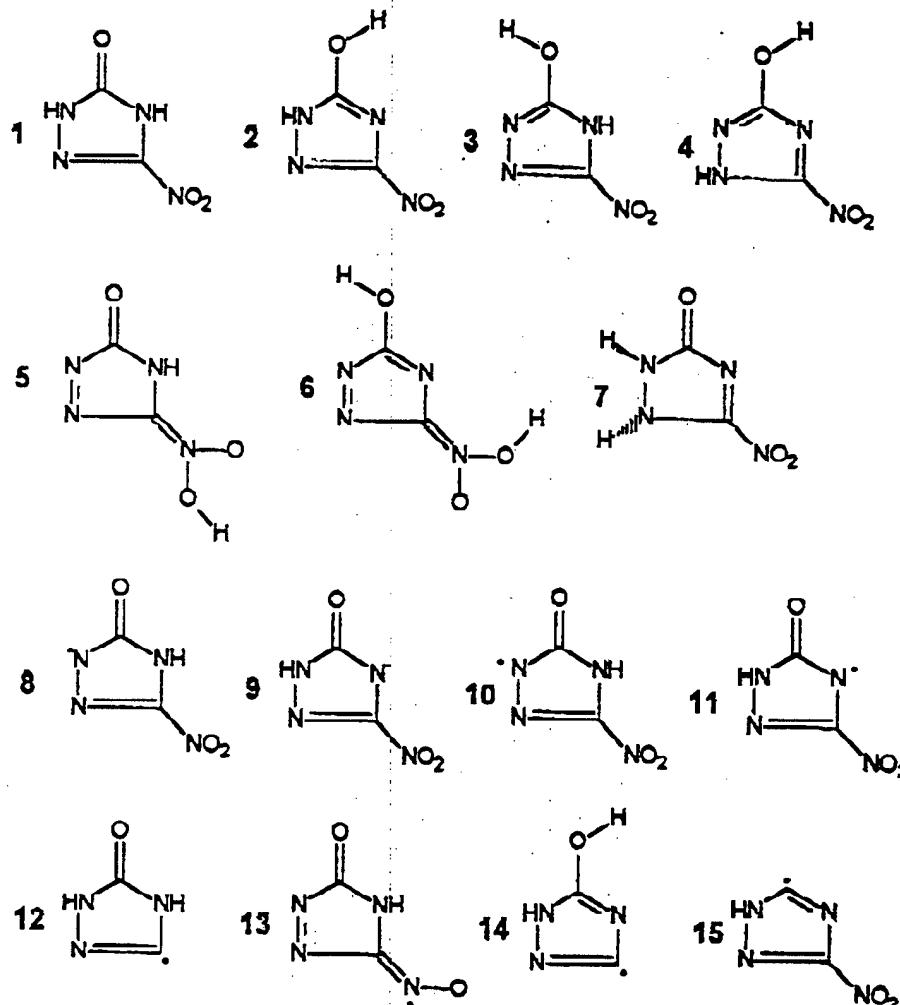
The rather small energy difference between NTO and the hydroxy tautomers **2** and **4** (4 kcal/mol at MP2/6-311+G** and 9 kcal/mol at B3LYP/6-311+G**) is explained to result from enhanced aromaticity in **2** and **4** compared with **1**. The enhanced aromaticity of these 1-H-1,2,4-triazole systems is evident from calculated C-N bond lengths, chemical shifts of the NH protons, and magnetical susceptibility anisotropies. Likewise the rather high acidity of NTO is explained in terms of the delocalized, aromatic character of the NTO anions. The computed proton affinity for the NTO anion is a low 321 kcal/mol (B3LYP/6-311+G** + ZPE).

The *aci*-nitro tautomers **5** and **6** are 30 kcal/mol less stable than NTO itself. The difference in stabilities is considerably larger than the 14 kcal/mol difference for the parent tautomeric system nitromethane/*aci*-nitromethane, which is probably a consequence of repulsion between the adjacent nitrogen sp^2 lone pairs in **5** and **6**. However, the *aci*-nitro tautomers are stable enough that they might play a part in the NTO decomposition.

The estimated N-II and C-NO₂ bond dissociation energies for NTO are respectively 93 and 70 kcal/mol, and that for the N-OH bond of the *aci*-nitro tautomer **5** is 38 kcal/mol. Our calculations

show that several tautomers of NTO are energetically accessible, and these may play a role in the condensed phase process, where they can be formed by a base-catalyzed mechanism. Some possible processes in the initial stages of NTO decomposition are bimolecular hydrogen atom transfers (in the condensed phase), C-NO₂ bond homolysis (at high temperatures or under conditions of shock or impact), and homolysis of the N-OH bond in the *aci*-nitro tautomers.

Investigated tautomers, radicals, en anions of NTO



2. RDX

Published in: N.J. Harris and K. Lammertsema, *Ab initio density functional computations of conformations and bond dissociation energies for hexahydro-1,3,5-trinitro-1,3,5-triazene*, *J. Am. Chem. Soc.* **119**, 6583 - 6589 (1997).

The more salient points are summarized:

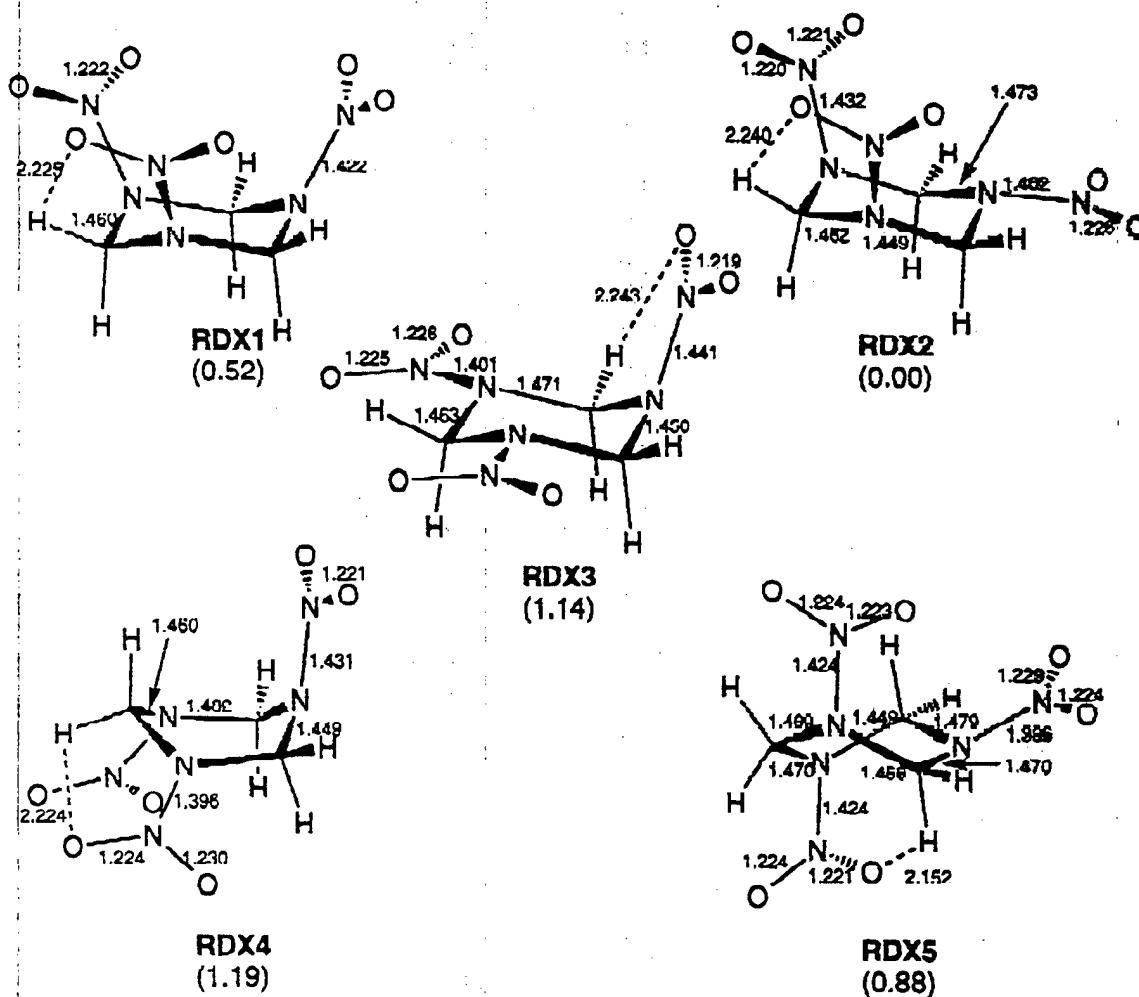
Ab initio computations are described of the conformers and bond dissociation energies of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) using the Becke3-Lee-Yang-Parr (B3LYP) nonlocal density functional and the standard 6-31G* and 6-311G** Gaussian basis sets. The B3LYP/6-311G**//B3LYP/6-31G* calculations suggest that the gas phase RDX molecule exists as a mixture of chair, boat, and twist conformers. The range in energy for these conformers is only about 1 kcal/mol. Three energy minimum chair conformations were found, differing in the axial/equatorial orientations of the nitro groups. Because of the low barrier for nitramine inversions, these three conformers should interconvert quite rapidly, giving an average chair structure with three equivalent nitro groups and C_{3v} symmetry. This is in agreement with the experimentally observed gas phase structure for RDX.

The observed conformation for crystalline RDX is similar to the conformation for the theoretical global energy minimum structure. Differences between observed and theoretical N-N bond lengths in RDX can be explained by crystal packing effects. Intermolecular electrostatic interactions in the solid state favor resonance donation of the amine lone pair into the NO_2 group, leading to shorter N-N bonds than in the gas phase. The RDX molecule has short intramolecular O-H contacts, which suggests that RDX can react by elimination of HONO.

The RDX nitrogen and carbon radicals have key roles in thermal decomposition of RDX. The B3LYP/6-311G** computed estimates for the C-H and the N- NO_2 dissociation energies (D_0) in RDX are respectively 85 and 42 kcal/mol. The latter value includes a correction for the tendency for B3LYP/6-311G** theory to underestimate N- NO_2 bond strengths by 6 kcal/mol compared with high level G2 theory. These are smaller than typical secondary C-H and N- NO_2 bond strengths in cyclohexane (96 kcal/mol) and DMNA (46 kcal/mol, our best estimate). Thus, the initiation of RDX decomposition by N- NO_2 homolysis and propagation of the decomposition by hydrogen atom abstractions should be facile processes.

The low N- NO_2 bond strength is a consequence of the sigma electron withdrawing NO_2 substituents in RDX. The weak C-H bond in RDX is similar in strength to an allylic or benzylic C-H bond, rather than a typical aliphatic C-H bond. The geometric features and atomic spin densities in the RDX carbon radical radical show it is partly delocalized into the adjacent NO_2 groups.

Five RDX conformers with B3LYP/6-31G* bond lengths (in Å) and B3LYP/6-311G** relative energies in kcal/mol.

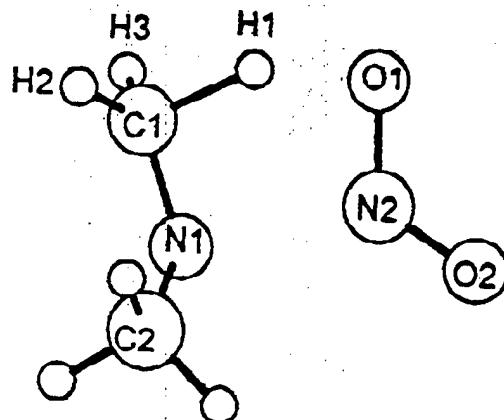


3. DMNA

Published in: N.J. Harris and K. Lammerink, *Ab initio density functional calculations of deuterium kinetic isotope effects for decomposition of dimethylnitramine*, J. Phys. Chem. A **101**, 1370 - 1373 (1997).

The more salient points are summarized:

Ab initio harmonic force fields were computed using the Becke3-Lee-Yang-Parr hybrid density functional with the standard 6-31G* basis set for dimethylnitramine, dimethylamino radical, and for the transition structure for five-center elimination of HONO from dimethylnitramine. These force fields were used to calculate the primary deuterium kinetic isotope effect for the HONO elimination, and the secondary isotope effect for the N-N bond homolysis of dimethylnitramine. The computed primary effect is $k^H/k^D = 4.21$, and the computed secondary effect is $k^H/k^D = 1.40$, both at 240 °C. Comparison with the experimentally observed isotopic effect of 1.57 for decomposition of dimethylnitramine-d6 in solution at 240 °C suggests a significant part of the observed effect is due to the secondary effect on N-N bond homolysis. Similar beta secondary deuterium isotope effects are expected for the N-NO₂ cleavages that initiate the decompositions of the nitramine explosives HMX and RDX. However, the experimentally observed isotope effects on the global decomposition rates of HMX and RDX in the condensed phase are best interpreted as primary effects operating on pathways that involve rate-determining C-H (or C-D) homolysis.



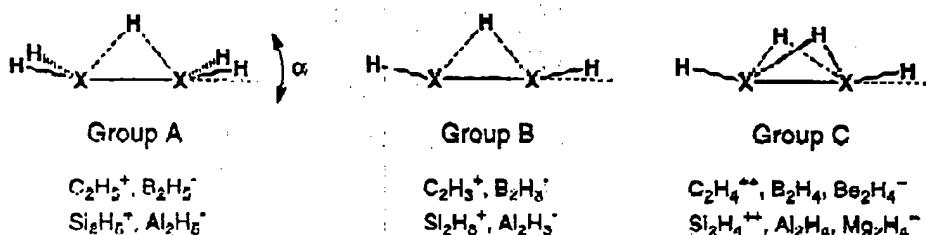
B3LYP/6-31G* transition structure for the elimination of HONO from dimethylnitramine.

4. 3c-2e Systems

Published in: K. Lammertsma and T. Ohwaria, *Three center - two electron systems. Origin of the tilting of its substituents.*, J. Am. Chem. Soc. 118, 7247 - 7254 (1996).

The more salient points are summarized:

This computational study, using MP2 6-311G** theory, is concerned with species that display the well-known three center - two electron bonding, all of which are either minima or transition structures. Particular emphasis is placed on the origin of the tilting of their H-substituents. Common bonding patterns are found for a broad group of such systems that include mono- and dications, mono- and dianions, and neutral molecules that contain eight different elements of the first and second row of the periodic table. The parent systems studied are $X_2H_3^{+/-}$ (C, B, Si, Al), $X_2H_5^{+/-}$ (C, B, Si, Al), and $X_2H_4^{2+/-}$ (C, B, Be, Si, Al, Mg). All but two of these (i.e., the ethyl cation and the ethylene dication) have their hydrogens on one side of a plane that contains both heavy elements. Accordingly, these elements have inverted geometries. The geometrical tilt angles of the terminal hydrogens can be quite significant. It is shown that the geometrical tilt angles between the X-H, and the X-X bonds of all the 3c-2e electron systems (anions, cations, dianions, dications, and neutrals containing eight different elements of the first and second row) become larger when the 3c-2e systems contain the heavier elements. Thus, the geometrical tilt angles correlate linearly with Allred & Rochow's elemental electronegativities. The bond lengths between the heavy elements also correlate with the tilt angles. The origin of these angles is traced to a mixing of the π (X-X) and σ (XH_2) orbitals. These two orbitals combined show a more diffuse nature in the H-bridging area. This is substantiated by the one-electron density analysis, which shows that the electronic structures of the 3c-2e have no tilt angles between the X-H and X-X bonds. Instead, molecular graphs show that the X-X bonds have convex curvatures. They further show that the bridging hydrogens have bond paths directly to the centers of these convex X-X bonds.



The three groups of this study, A: $X_2H_3^{+/-}$, B: $X_2H_5^{+/-}$, and C: $X_2H_4^{2+/-}$.

5. Protonation

Published in: N.J. Harris, T. Ohwada, and K. Lammertsma, *Protonation energies in fluorosulfonic acid using ab initio self consistent reaction field theory*, *J. Comput. Chem.* **19**, 250 - 257 (1998).

The more salient points are summarized:

Electrostatic solvation free energies were computed for several small neutral bases and their conjugate acids using a continuum solvation model, called the Self-Consistent Isodensity Polarizable Continuum Model (SCIPCM). The solvation energies were computed at the restricted Hartree-Fock (RHF) and at the second-order Møller-Plesset (MP2) levels of theory, as well as with the Becke3-Lee-Yang-Parr (B3LYP) density functional theory, using the standard 6-31G** Gaussian basis set. The RHF solvation energies are similar to those computed at the correlated MP2 and B3LYP theoretical levels.

A model for computing protonation enthalpies for neutral bases in fluorosulfonic acid solvent leads to the equation $\Delta H_{\text{prot,HSO}_3\text{F}}(\text{B}) = -\text{PA}(\text{B}) + \Delta E_i(\text{BH}^+) - \Delta E_i(\text{B}) + \text{CONSTANT}$, where $\text{PA}(\text{B})$ is the gas phase proton affinity for base B , $\Delta E_i(\text{BH}^+)$ is the SCIPCM solvation energy for the conjugate acid, and $\Delta E_i(\text{B})$ is the solvation energy for the base. A fit to experimental values of $\Delta H_{\text{prot,HSO}_3\text{F}}(\text{B})$ for ten neutral bases (H_2O , MeOH , Me_2O , H_2S , MeSH , Me_2S , NH_3 , MeNH_2 , Me_2NH , and PH_3) gives $\text{CONSTANT} = 238.4 \pm 2.9$ kcal/mol, when ΔE_i is computed using the 0.0004 e_Bohr⁻³ isodensity surface for defining the solute cavity, at the RHF/6-31G** level. The comparison with available experimental data for aqueous solvation of amines and ammonium ions suggests the SCIPCM energies are quite reasonable, especially after correcting experimental data for nonelectrostatic contributions to the solvation energy. Importantly, the SCIPCM solvation energies reproduce the expected trend of decreased solvation energy for substitution of X-H by X-CH_3 . Our model for computing enthalpies for protonation of neutral bases in fluorosulfonic acid should give enthalpies accurate to within 5 kcal/mol for second-row bases (thioethers and phosphines) and 2 kcal/mol for first-row bases (amines, ethers, carbonyl compounds).

The model predicts that for carbon monoxide $\Delta H_{\text{prot,HSO}_3\text{F}}(\text{CO}) = 10$ kcal/mol. Thus protonation of CO is endothermic, and the conjugate acid HCO^+ (formyl cation) behaves as a strong acid in fluorosulfonic acid. Thus, the model allows prediction of protonation enthalpies for other bases like carbon monoxide that are incompletely protonated in superacids.

6. Tautomerism

Attachment A: J. A. Long, N. J. Harris, and K. Lammersema, *Formaldehyde oxime \rightleftharpoons nitrosomethane tautomerism*.

The more salient points are summarized:

Formaldehyde oxime \rightleftharpoons nitrosomethane tautomerism, isomeric nitrone, and their common cations and anions were studied with Gaussian-2 theory using MP2(full)/6-31G* geometries and with density functional theory using B3LYP/6-311+G**. Geometrical parameters, harmonic vibrational frequencies, relative stabilities, conformational stabilities, and ionization energies are compared with experimental gas phase data when available. The formaldehyde oxime \rightleftharpoons nitrosomethane tautomerism are compared with the amide \rightleftharpoons imidol, imine \rightleftharpoons enamine, keto \rightleftharpoons enol, and nitro \rightleftharpoons aci-nitro tautomeric processes. Solvent effects are estimated by the self consistent isodensity polarizable continuum model (SCIPCM). The influence of hydrogen bonding interactions with the solvent is addressed by including two water molecules. In the final evaluation, formaldehyde oxime 1 is 15.8 kcal/mol more stable than nitrosomethane 3 when the aqueous solvation correction of 3.8 kcal/mol is applied to the G2 energies. Unsolvated formaldehyde oxime is estimated to be 11.1 kcal/mol more stable than nitrone 4. The estimated gas phase ionization energies (G2) are 362.5 kcal/mol for formaldehyde oxime, 350.6 kcal/mol for nitrosomethane, and 351.4 kcal/mol for nitrone. The corresponding protonation energies are 191.6, 181.4, and 202.8 kcal/mol, respectively.

Relative energies calculated with R3LYP/6-31G* are generally in very good agreement with those obtained with G2 theory. Likewise, their geometries and harmonic vibrational frequencies compare well with those obtained with MP2(full)/6-31G*.

